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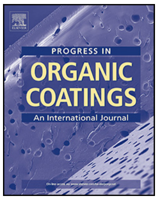

Diffusion of surface-active amphiphiles in silicone-based fouling-release coatings

A. Camós Noguer[a,b], S.M. Olsen[b], S. Hvilsted[a], S. Kiil[a,*]

[a] *Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Building 229, 2800 Kgs. Lyngby, Denmark*
[b] *Department of Fouling Release Systems, Hempel A/S, Lundtoftegårdsvej 91, 2800 Kgs. Lyngby, Denmark*

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ABSTRACT

Amphiphiles (i.e. amphiphilic molecules such as surfactants, block copolymers and similar compounds) are used in small amounts to modify the surface properties of polymeric materials. In silicone fouling-release coatings, PEG-based amphiphiles are added to provide biofouling-resistance. The success of this approach relies on the ability of the amphiphiles to diffuse through the coating film and cover the surface of the coating.

A novel method for the measurement of diffusion coefficients of PEG-based amphiphiles of different chemistries in PDMS-based coatings is presented here. The diffusion coefficient of the amphiphiles shows a weak dependency on their molecular weight, although this dependency is much less pronounced than for other rubbery polymeric materials. The biofouling-resistance properties in fouling-release coatings were also studied for these amphiphiles. It was found that the diffusion coefficient does not have any influence on the biofouling-resistance results for the studied compounds. Instead, the chemistry of the hydrophobic block of the amphiphiles is much more significant, with PEG-PDMS block copolymers showing the best properties among the studied compounds.

1. Introduction

Additives are usually used to modify the processing and final properties of polymeric materials. Plasticizers, antioxidants and flame retardants are examples of such additives [1]. The use of surface-active additives has gained interest as an easy, cheap and fast way to modify the surface properties of polymeric materials. These surface-active compounds (usually block copolymers) migrate to the material surface and cover it, thus significantly changing the surface properties of the material with a very small impact on its bulk properties [2,3]. For example, James et al. [4] added a fluoro-modified polystyrene additive to a polyester to improve its stability against hydrolysis. Miyata et al. [5] added polydimethylsiloxane- (PDMS) based copolymer additives to a PDMS membrane in order to improve the ethanol permeation selectivity of the membrane. Likewise, Wu and Hjort [6] added tri-block poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) (PEG-PPG-PEG) copolymers to PDMS to supress nonspecific protein adsorption on the surface of microfluidic devices. Furthermore, Røn et al. [7] used poly(acrylic acid)- and poly(ethylene glycol)-based block copolymers to improve the lubricity of PDMS surfaces. In the field of coatings, surface-active additives have been employed for a range of purposes: as stabilizing agents for single-wall carbon nanotubes [8] and for bactericidal silver ion delivery in polyurethane-based coatings [9]. Moreover, they have been used to increase the colloidal stability in emulsion polymerization for latex coatings [10] and to improve the flowing and levelling properties of polyurethane coatings [11] to mention some examples.

Irrespective of the intended use of these surface-active compounds, they have a tendency to diffuse and migrate to interfaces [3]. Siloxane additives used as flow agents migrate to the surface of automotive clearcoats, compromising the adhesion of pressure-sensitive adhesives on the clearcoats [12], and it has been reported [13] that the surfactants used in latex-based coatings can exudate to the interfaces of the latex film, giving rise to optical and adhesion problems. On the other hand, the diffusion of surface-active additives to the coatings' interfaces has beneficial effects in other cases. Polyfluorinated surfactants have been used in coatings for food packaging to provide water and oil repellency [14]. Similarly, Rixens et al. [15] used phosponic ester- and phosphonic acid-modified polymers to increase the adhesion of vinylidene chloride-methyl acrylate coatings on metal substrates. Moreover, PEG-based copolymers have been used as additives for PDMS-based fouling-release coatings to decrease biofouling and barnacle adhesion [16].

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[*] Corresponding author.
E-mail addresses: alno@kt.dtu.dk (A. Camós Noguer), stmo@hempel.com (S.M. Olsen), sk@kt.dtu.dk (S. Kiil).

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Table 1
Chemical composition and properties of the amphiphiles used and the diffusion coefficients obtained. Structure (where A represents the hydrophilic block and B the hydrophobic block), molecular weight (M_w), number of poly(ethylene glycol) (PEG) units, hydrophilic-lipophilic balance (HLB) and diffusion coefficient (D) are shown for each amphiphile. Note that they have been ordered according to the chemistry of the hydrophobic block of the amphiphile.

Chemistry of the hydrophobic block	Amphiphile	Amphiphile structure	M_w (g/mol)	Number of PEG units in the hydrophilic block	HLB[e]	$D\ (m^2/s) \cdot 10^{12}$	Coating number (see Fig. 10)
Alkyl	Brij O10	AB	720	10	12,5	15,9 ± 1,1	1
Alkyl	Lumulse POE(7) GML	AB	580	7	10,5	21,6 ± 8,3	2
Alkyl	Serdox NES 7	AB	570	7	12	35,5 ± 12,8	3
Alkyl	Tween 85	–	1840[b]	20[c]	11[b]	2,2 ± 0,4	4
Alkyl	PEG 12 stearate	AB	820	12	13	12,5 ± 0,8	5
Alkyl + Aryl	Sapogenat T 080	AB	620	8	11,5	19,6 ± 7,5	6
Alkyl + Aryl	Sapogenat T 130	AB	840	13	13,5	5,6 ± 2,4	7
Alkyl + Aryl	Triton X-100	AB	610	10	13,5	9,3 ± 2,3	8
Alkyl + Aryl	Igepal CO-720	AB	730	12	14	10,0 ± 2,6	9
PDMS	Copolymer 1	AB	660	8	11	8,8 ± 0,3	10
PDMS	Copolymer 2	Grafted	3940	10[d]	8	3,2 ± 0,5	11
PDMS	Copolymer 3	ABA	1960	10[d]	10,5	3,4 ± 1,6	12
–	PEG400	A	400	8	–	–	13[f]
–	–[a]	–	–	–	–	–	14[f]

[a] No additive was used for this coating.
[b] The value provided by the supplier was used.
[c] Total number of PEG units in the molecule, distributed in 4 different branches.
[d] Number of PEG units in each block/branch.
[e] Estimated using Eq. (4).
[f] Coatings only used as references for contact angle and static immersion tests.

Biofouling is the undesired accumulation of organisms on immersed surfaces such as biomedical implants, biosensors and ships [17]. The use of different kinds of surface-active compounds to decrease the amount of biofouling on fouling-release coatings is widespread. Various patents [18–24] and articles [2,25–28] in the field describe the use of both reactive and non-reactive amphiphilic copolymers in fouling-release coatings, mainly based on fluorinated, siloxane and oxyalkylane moieties. Among them, poly(ethylene glycol) has shown promising results in the biomedical field regarding fouling-resistance properties [29]. Different methods have been used to functionalize surfaces with PEG. Besides adding PEG-based surface-active compounds to change the surface properties of PDMS films, PEG has also been covalently grafted or physically adsorbed on different substrates [29,30]. However, these methods are more expensive and are not applicable for big-scale productions like fouling-release coatings for ships. Therefore, it is believed that incorporating PEG-based copolymers and exploiting their surface-activity is the most effective way to obtain long-term effective fouling-release coatings. The proposed working mechanism for these additives is based on the segregation and coverage of the coating surface. The driving force leading to the surface segregation of different kinds of polymer additives has been previously studied. Inutsuka et al. [31] investigated the segregation of PDMS-b-PEG copolymers in PDMS films under water. The migration driving force was attributed to the enthalpic gain associated with the solvation of the PEG block of the copolymer molecules at the film surface. Lee and Archer [3,32] studied the segregation of different additives in polystyrene (PS) hosts, and similarly found the decrease in the system's energy one of the main driving forces. Regarding the covering of the coating surface, the hydrophobic block of the copolymer acts as an anchor on the surface, while the PEG block provides the fouling-release protection [33,34]. Therefore, the long-term fouling-release protection properties of these coatings are dictated both by the hydrophobic and the hydrophilic blocks of these amphiphilic additives.

The characterization of surface segregation/enrichment in polymeric materials has been achieved by different means. Radioactive labelling [35], infrared microdensiometry [35], fluorescence tracing [36], time-of-flight secondary ion mass spectrometry (ToF-SIMS) [37] and X-ray photoelectron spectroscopy (XPS) [38] have been used with successful results. Similarly, the diffusion of different migrants in polymer hosts has also been studied by methods such as Raman spectroscopy [39], gas chromatography (GC) [39] and infrared spectroscopy (IR) [40] among others.

In this paper, the functionalization of silicone-based fouling-release coatings by addition of PEG-based amphiphiles is studied. An amphiphile is a molecule having different blocks, which provide both hydrophobic and hydrophilic properties to the molecule. Amphiphiles with three different kinds of hydrophobic blocks have been used, while PEG has been kept as hydrophilic block for all of them. The three hydrophobic blocks chosen have been: (1) alkyl hydrocarbon chains, (2) alkyl hydrocarbon chains connected to an aryl group and (3) PDMS chains, with different molecular weight and structure. A new procedure, based on a time lag method combined with an optical tensiometer, is used to study the diffusion of these amphiphiles through crosslinked PDMS films for fouling-release purposes. The use of time lag methods has previously been reported in the literature to obtain diffusion coefficients of different compounds in films. For example, Stewart et al. [41] measured the diffusivity of acids through thin polymer films below and above the glass transition temperature (T_g). Valente et al. [42], studied the diffusion of sodium dodecyl sulphate (SDS) through cellulose esters membranes, and Faucher et al. [43] analysed diffusion phenomena of sodium lauryl sulphate (SLS) through rat stratum corneum. In contrast with other methods that usually require sample preparation, extraction methods, vacuum and/or long waiting times, diffusion coefficients for relatively high molecular weight (M_W) amphiphiles and block copolymers can be obtained in an easy and rapid way by using the method presented in this work. Experimental diffusion coefficients are obtained for such molecules in crosslinked PDMS films. In addition, the diffusion coefficients obtained are compared to literature values of other diffusing molecules and polymers. The effect of the diffusant chemistry and M_W on the diffusion of these compounds within the coating film and the influence on the final fouling-resistance properties of the coatings are discussed.

2. Materials and methods

2.1. Materials

Silanol terminated PDMS (4000 cSt) was received from Dow Corning and vinyl tris(methyl ethyl ketoxime) silane from Evonik.